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1 **Raman spectroscopic study of the uranyl selenite mineral demesmaekerite**



3
4 **Ray L. Frost,^{1*} Jiří Čejka^{1,2} and Marilla J. Dickfos¹**

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6 ¹ Inorganic Materials Research Program, School of Physical and Chemical Sciences,
7 Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001,
8 Australia.

9
10 ² National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

11
12 **Abstract**

13
14 **The Raman spectrum of uranyl selenite mineral demesmaekerite was**
15 **studied, complemented by infrared spectrum, and tentatively**
16 **interpreted. Stretching and bending vibrations of $(\text{UO}_2)^{2+}$, $(\text{SeO}_3)^{2-}$ and**
17 **OH groupings were attributed to observed bands. U-O bond lengths in**
18 **uranyl and O-H...O hydrogen bond lengths were calculated from**
19 **Raman and/or infrared spectra and compared with published data.**

20
21 **KEYWORDS:** demesmaekerite, uranyl selenite, Raman spectroscopy, U-O bond
22 length, O-H...O bond lengths

23
24 **INTRODUCTION**

25
26 Oxoanions possessing a stereochemically active lone pair of electrons have a
27 prosperity for aligning in the solid state to yield polar structures¹. The family of
28 U(VI) compounds with oxoanions of Se(IV) is therefore rapidly expanding².
29 Uranyl minerals, containing the selenite anion $(\text{SeO}_3)^{2-}$ are known³: derriksite
30 ⁴, demesmaekerite⁵, guilleminite⁶, marthozite⁷, haynesite⁸, piretite⁹ and larisaite¹⁰.
31 According to Burns¹¹⁻¹³, the majority of natural and synthetic uranyl compounds are
32 layered. In the compounds, uranyl ions are coordinated to four, five or six oxygens in
33 their equatorial plane thus forming UO_2O_4 tetragonal, UO_2O_5 pentagonal and UO_2O_6

34 hexagonal dipyramidal uranyl coordination polyhedra, UO₂O₅ pentagonal dipyramidal
35 coordination polyhedra being most frequent. Guilleminite, marthozite, larisaite and
36 probably also haynesite and piretite are characterized by [(UO₂)₃(O,OH)₂(SeO₃)₂]
37 sheets formed from chains of edge-sharing UO₂O₅ pentagonal dipyramids and UO₂O₆
38 hexagonal dipyramids that are bridged by (SeO₃)²⁻ anions. These sheets exhibit the
39 phosphuranylite anion sheet topology. Derriksite and demesmaekerite are
40 characterized by formation of one-dimensional chains of UO₂O₄ (derriksite) and
41 UO₂O₅ (demesmaekerite) dipyramids bridged by (SeO₃)²⁻ anions.

42

43 According to Finch and Murakami¹⁴, uranyl selenite minerals occur where Se-
44 bearing sulfide minerals are undergoing oxidation and dissolution. Demesmaekerite,
45 derriksite, guilleminite and marthozite are from the Musonoi Cu-Co mine, near
46 Kalwezi, Katanga Province, Democratic Republic of Congo, piretite and also
47 guilleminite from Shinkolobwe, Katanga, Democratic Republic of Congo, haynesite
48 and larisaite from the Repete mine, San Juan Co., Utah, U.S.A.^{3,10}. Anhydrous
49 and/or hydrated uranyl selenites (Ca, Sr, Ba, Ag, Pb) were prepared and their
50 structures were determined^{1,2,15}.

51

52

53 Triclinic demesmaekerite, Pb₂Cu₅(UO₂)₂(SeO₃)₆(OH)₆·2H₂O
54 , a 11.955(5), b 10.039(4), c 5.639(2) Å, α 89.78(4), β 100.36(4), γ 91.34(4) °, space
55 group *P*-1, Z = 1, possesses one symmetrically distinct U⁶⁺ in the form of uranyl,
56 (UO₂)²⁺, and two symmetrically distinct Se⁴⁺ in the form of (SeO₃)²⁻, three
57 symmetrically distinct Cu²⁺, three symmetrically distinct hydroxyl ions and one
58 symmetrically distinct water molecule¹⁶. The demesmaekerite crystal structure is
59 characterized by chains. The chains contain UO₂O₅ pentagonal dipyramids as well as
60 (SeO₃)²⁻ triangles that are distorted by the presence of a lone pair of electrons on the
61 Se⁴⁺ cation. Adjacent UO₂O₅ pentagonal dipyramidal uranyl coordination polyhedra
62 are linked by sharing corners with (SeO₃)²⁻ triangles. Each UO₂O₅ polyhedron is
63 linked to four (SeO₃)²⁻ triangles. The fifth equatorial ligand of the UO₂O₅ pentagonal
64 dipyramid is shared with a (SeO₃)²⁻ triangle that is one-connected to the chain. Two of
65 three CuO₂O₄ polyhedra are distorted due to the Jahn-Teller effect. The CuO₂X₄

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

66 octahedra link by sharing edges to form zigzag chains, parallel to c axis; adjacent
67 chains of CuO_2X_4 octahedra link by corner-sharing to form sheets parallel to (010).
68 The structure contains a single symmetrically distinct Pb^{2+}X_6 polyhedron, linked to
69 the sheet of Cu^{2+}X_6 octahedra ($\text{X} = \text{O}, \text{OH}, \text{H}_2\text{O}$). Thus formed $\text{PbX}_6\text{-CuX}_6$ sheets are
70 cross-linked by the uranyl selenite chains ^{11,16,17}.

71

72 Infrared spectra of some synthetic anhydrous and hydrated uranyl selenites
73 were presented and partially tentatively interpreted ^{2,15}. Infrared spectra of the uranyl
74 selenite minerals piretite ⁹, haynesite ¹⁸ and larisaitite ¹⁰ and Raman spectra of
75 haynesite ¹⁹, marthozite [Frost *et al.* JRS submitted], and guilleminite [Frost *et al.*
76 submitted] were also studied.

77

78 The aim of this paper is the study of Raman spectra of the natural uranyl
79 selenite demesmaeckerite complemented by infrared spectrum of demesmaeckerite. The
80 paper is a part of systematic research of secondary minerals formed in the oxidation
81 zone, inclusive uranyl minerals originating during hydration-oxidation weathering of
82 primary uranium minerals such as uraninite. Raman spectroscopy was proven most
83 useful for the characterisation of secondary uranyl containing minerals ¹⁹⁻²⁵.

84

85 **EXPERIMENTAL**

86

87 ***Mineral***

88

89 The mineral demesmaeckerite originated from the Musonoi Mine, Zaire, Congo and
90 was obtained through the Mineralogical research Company. The composition of the
91 mineral has been published by Anthony *et al.* (page 181) ³.

92

93 ***Raman microprobe spectroscopy***

94

95 The crystals of demesmaeckerite were placed and orientated on the stage of an
96 Olympus BHSM microscope, equipped with 10x and 50x objectives which was part
97 of a Renishaw 1000 Raman microscope system, also including a monochromator,
98 filter system and Charge Coupled Device (CCD). Raman spectra were excited by a
99 HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000

100 cm^{-1} . Repeated acquisition using the highest magnification was accumulated to
101 improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of
102 a silicon wafer. Details of the technique have been published by the authors.^{19,26-30}
103

104 Spectroscopic manipulation such as baseline adjustment, smoothing and
105 normalisation were performed using the Spectracalc software package GRAMS
106 (Galactic Industries Corporation, NH, USA). Band component analysis was
107 undertaken using the Jandel 'Peakfit' software package, which enabled the type of
108 fitting function to be selected and allows specific parameters to be fixed or varied
109 accordingly. Band fitting was done using a Gauss-Lorentz cross-product function with
110 the minimum number of component bands for the fitting process. The Gauss-Lorentz
111 ratio was maintained at values greater than 0.7 and fitting was undertaken until
112 reproducible results were obtained with squared correlations of r^2 greater than 0.995.
113 Further details on the manipulation of the data has been published³¹⁻⁴¹.
114

115 *Infrared Spectroscopy*

116

117 Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer
118 with a smart endurance single bounce diamond ATR cell. Spectra over the $4000\text{--}525$
119 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1}
120 and a mirror velocity of 0.6329 cm/s . Spectral manipulation such as baseline
121 adjustment, smoothing and normalisation was performed using the GRAMS®
122 software package (Galactic Industries Corporation, Salem, NH, USA).
123

124 **RESULTS AND DISCUSSION**

125

126 The free linear uranyl group $(\text{UO}_2)^{2+}$, symmetry $D_{\infty h}$, has four normal
127 vibrations but only three fundamental bands: the ν_1 symmetric stretching vibration
128 (approximately $900\text{--}700 \text{ cm}^{-1}$), only Raman active; the ν_2 (δ) double degenerate
129 bending vibration (approximately $300\text{--}200 \text{ cm}^{-1}$), only infrared active; the ν_3
130 antisymmetric stretching vibration (approximately $1000\text{--}850 \text{ cm}^{-1}$), only infrared
131 active. Distortion of the uranyl group or change in the local symmetry can result in the

132 removal of the degeneracy and therefore Raman activation of the ν_2 mode, infrared
133 activation of the ν_1 mode, and Raman activation of the ν_3 mode^{18,19}.

134

135 The chemistry of the selenite and selenite containing compounds resembles
136 the chemistry of the sulphite ion and its compounds. The symmetry of the selenite ion
137 is similar to that of sulphite, which is tetrahedral with one vacant orbital thus making
138 C_{3v} symmetry⁴². The selenite ion $(\text{SeO}_3)^{2-}$ thus has four fundamentals: the ν_1
139 symmetric stretching vibration (approximately 790-806 or 760-855 cm^{-1}); the ν_2
140 symmetric bending vibration (approximately 430-461 cm^{-1}); the doubly degenerate ν_3
141 antisymmetric stretching vibration (approximately 714-769 or 680-775 cm^{-1}); the ν_4
142 doubly degenerate antisymmetric bending vibration (approximately 387-418 cm^{-1}).
143 All vibrations are Raman and infrared active [Frost *et al.*, JRS, submitted].

144

145 In the crystal structure of demesmaeckerite, there are one symmetrically distinct
146 uranyl ion $(\text{UO}_2)^{2+}$ and two symmetrically distinct $(\text{SeO}_3)^{2-}$ ions¹⁶. Raman and
147 infrared spectra of demesmaeckerite are given in Figs 1-7.

148

149

150 Raman band at 822 cm^{-1} and infrared band at 819 cm^{-1} were attributed to the
151 $\nu_1 (\text{UO}_2)^{2+}$ symmetric stretching vibration. No Raman signal was observed related to
152 the $\nu_3 (\text{UO}_2)^{2+}$ antisymmetric stretching vibration. Infrared band at 878 cm^{-1} was
153 assigned to the $\nu_3 (\text{UO}_2)^{2+}$ vibration. These wavenumbers are comparable with those
154 observed for the Raman and infrared spectra of other uranyl selenite minerals^{9,10,18,19}.
155 Observed wavenumbers assigned to the ν_1 and $\nu_3 (\text{UO}_2)^{2+}$ were used for calculation of
156 U-O bond lengths in uranyls with two empirical relations by Bartlett and Cooney⁴³.
157 Obtained results ($\text{\AA}/\text{cm}^{-1}$) 1.789/822, 1.792/819 and 1.801/878 are somewhat higher
158 than the average value 1.745 \AA inferred from the X-ray single crystal structure
159 analysis of demesmaeckerite¹⁶. The $\nu_1 (\text{UO}_2)^{2+}$ assignment close to the $\nu_3 (\text{UO}_2)^{2+}$
160 ν_1/ν_3 860-883/880-900 cm^{-1} in some synthetic potassium and ammonium uranyl
161 selenites, published by Khandelwal and Verma⁴⁴ does not seem to be correct. $\nu_1 =$
162 $0.94\nu_3 \text{ cm}^{-1}$ or $\nu_1 = 0.89\nu_3 + 21 \text{ cm}^{-1}$, i. e. 827/880 and 846/900 cm^{-1} or 804/880 and
163 822/900 cm^{-1} [e.g. Čejka¹⁸].

164

165 Raman band at 756 cm^{-1} and infrared bands at 778 and 799 cm^{-1} were assigned
166 to the $\nu_1(\text{SeO}_3)^{2-}$ symmetric stretching vibrations, and those at 719 cm^{-1} and $673, 693,$
167 $712, 731$ and 750 cm^{-1} , respectively, to the doubly degenerate $\nu_3(\text{SeO}_3)^{2-}$
168 antisymmetric stretching vibrations. Raman bands at 450 and 432 cm^{-1} were attributed
169 to the $\nu_2(\text{SeO}_3)^{2-}$ symmetric bending vibrations, while those at 351 and 432 cm^{-1} to
170 the doubly degenerate $\nu_4(\text{SeO}_3)^{2-}$ antisymmetric bending vibrations. Raman bands at
171 295 and 269 cm^{-1} are connected with the $\nu_2(\delta)(\text{UO}_2)^{2+}$ bending vibrations and those
172 at $215, 178, 151$ and 114 cm^{-1} to the lattice vibrations.

173

174 In the region of $1050 - 1200\text{ cm}^{-1}$, a Raman band at 1062 cm^{-1} and infrared
175 bands at 1033 and 1049 cm^{-1} were observed, which are assigned to the $\delta\text{ U-OH}$
176 bending vibrations, and those at 1095 cm^{-1} (Raman) and $1090, 1122, 1167$ and 1194
177 cm^{-1} (IR) may be attributed to the $\nu_1 + \nu_2(\text{UO}_2)^{2+}$ and/or $\nu_3 + \nu_2(\text{UO}_2)^{2+}$ combination
178 bands. Raman and infrared bands in the range $1348 - 1506\text{ cm}^{-1}$ may be assigned to
179 overtones and/or combination bands.

180

181 Raman bands at 3319 and 3382 cm^{-1} and infrared bands at $3239, 3317, 3490$
182 and 3491 cm^{-1} are assigned to the $\nu\text{ OH}$ stretching vibrations. U-O...O bond lengths
183 of hydrogen bonds expected in the crystal structure of demesmaekerite were inferred
184 with Libowitzky's empirical relation⁴⁵ ($\text{\AA}/\text{cm}^{-1}$): $2.76/3319$ and $2.79/3382$
185 (Raman), $2.72/3239, 2.76/3317, 2.80/3405$ and $2.89/3491$ (IR). These values are close
186 to those inferred from the X-ray single crystal structure analysis¹⁶. The role of water
187 molecules is not clear. According to Ginderow and Cesbron¹⁶, water molecules are
188 free or only very weakly hydrogen bonded. However, corresponding bands were
189 observed neither in Raman nor infrared spectrum of demesmaekerite.

190

191 **Conclusions**

192

193 Raman spectrum of uranyl selenite mineral demesmaekerite,
194 $\text{Pb}_2\text{Cu}_5[(\text{UO}_2)_2(\text{SeO}_3)_6](\text{OH})_6 \cdot 2\text{H}_2\text{O}$, was studied and complemented by its infrared
195 spectrum. Observed bands were tentatively attributed to the stretching and bending
196 vibrations of uranyl and selenite ions and OH groupings. Observed spectra are
197 comparable with those of other uranyl selenite minerals. U-O bond lengths in uranyls

198 and O-H...O hydrogen bond lengths were calculated from the Raman and infrared
199 spectra. Obtained U-O bond lengths are somewhat higher than those inferred from the
200 X-ray single crystal structure analysis of demesmaekerite. Hydrogen bond lengths are
201 comparable with those from the structure analysis of demesmaekerite; however the
202 role of water molecules cannot be inferred from the spectra.

203

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205

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208 Chemical Sciences is gratefully acknowledged. The Australian Research Council
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210

211

212 **References**

213

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276
277
278

279 **List of Fig.s**

280

281 **Fig. 1 Raman spectrum of desmakeaerite in the 700 to 1600 cm^{-1} region.**

282

283 **Fig. 2 Raman spectrum of desmakeaerite in the 100 to 700 cm^{-1} region.**

284

285 **Fig. 3 Raman spectrum of desmakeaerite in the 3200 to 3500 cm^{-1} region.**

286

287 **Fig. 4 Infrared spectrum of desmakeaerite in the 850 to 1250 cm^{-1} region.**

288

289 **Fig. 5 Infrared spectrum of desmakeaerite in the 550 to 850 cm^{-1} region.**

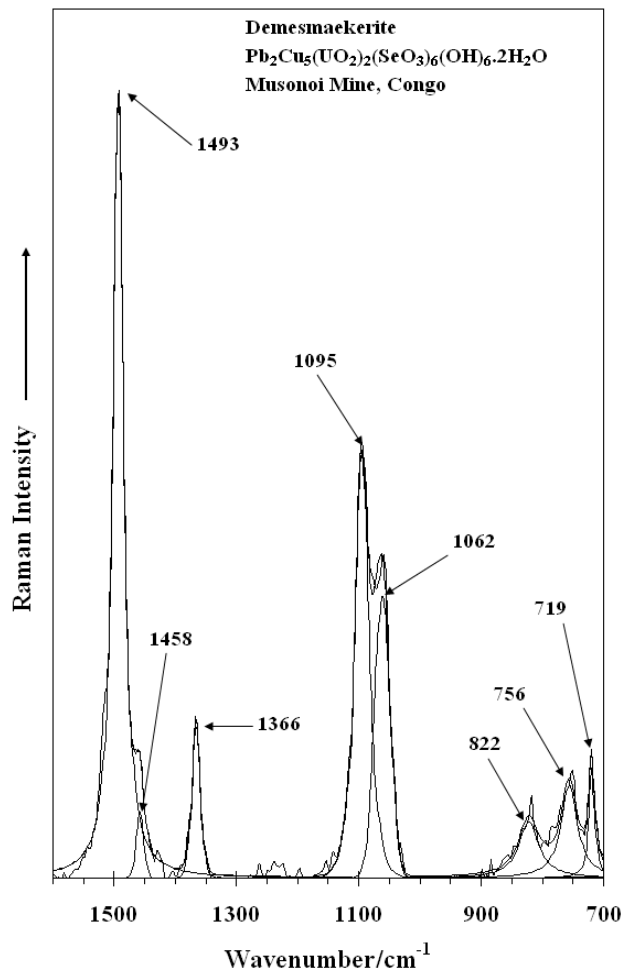
290

291 **Fig. 6 Infrared spectrum of desmakeaerite in the 1300 to 1600 cm^{-1} region.**

292

293 **Fig. 7 Infrared spectrum of desmakeaerite in the 2800 to 3800 cm^{-1} region.**

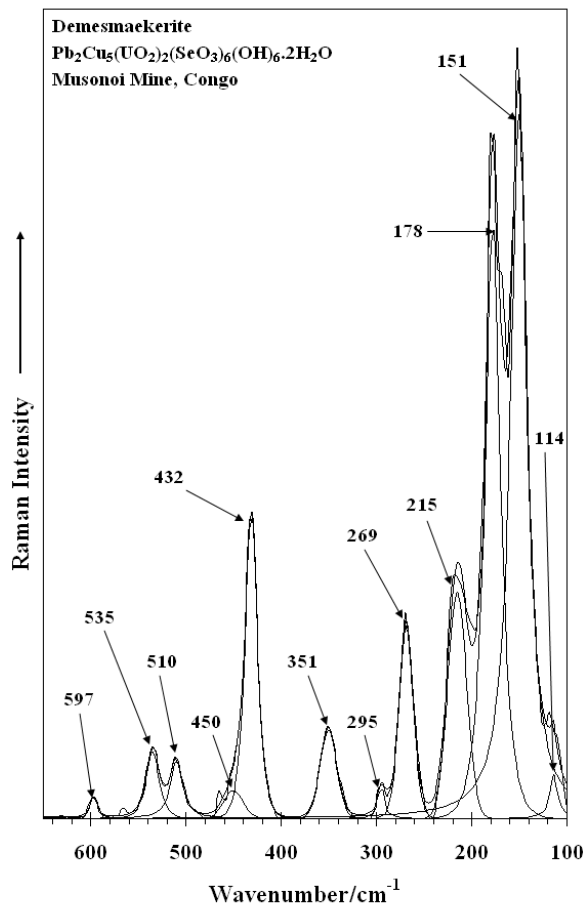
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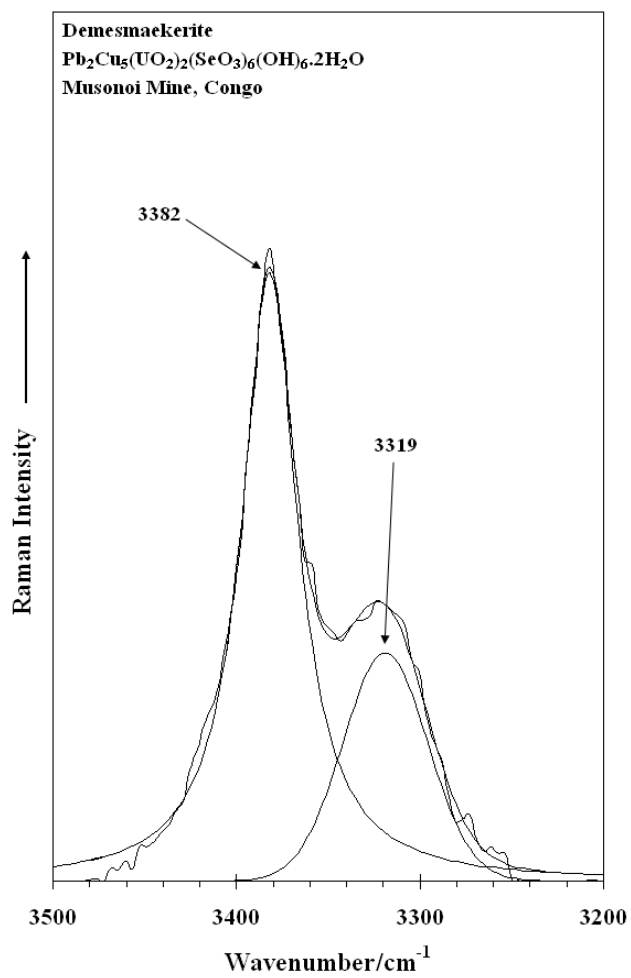
298 **Fig. 1**



299

300

301 **Fig. 2**

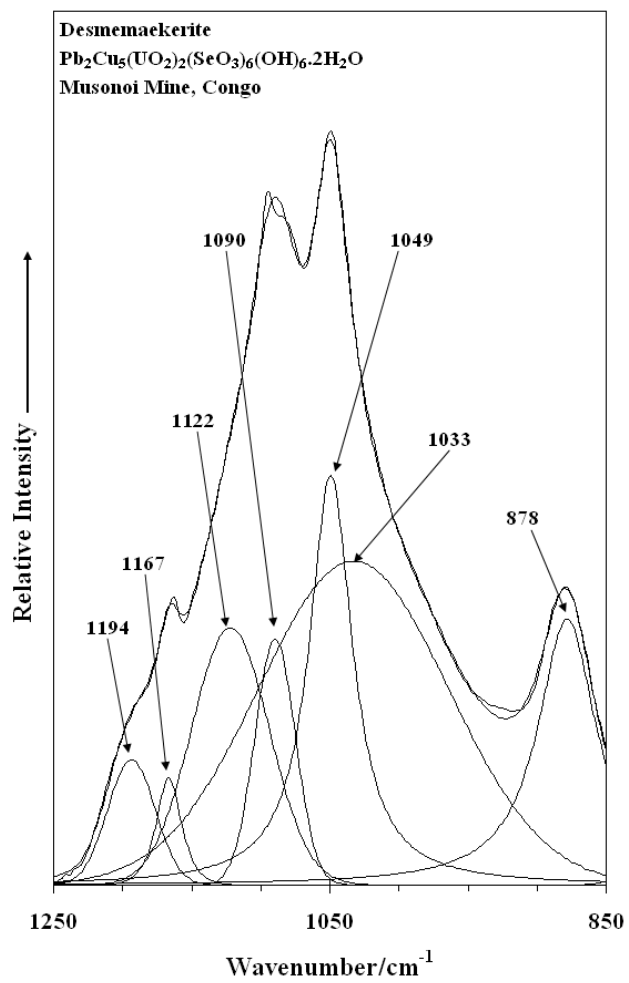


302

303

304 **Fig. 3**

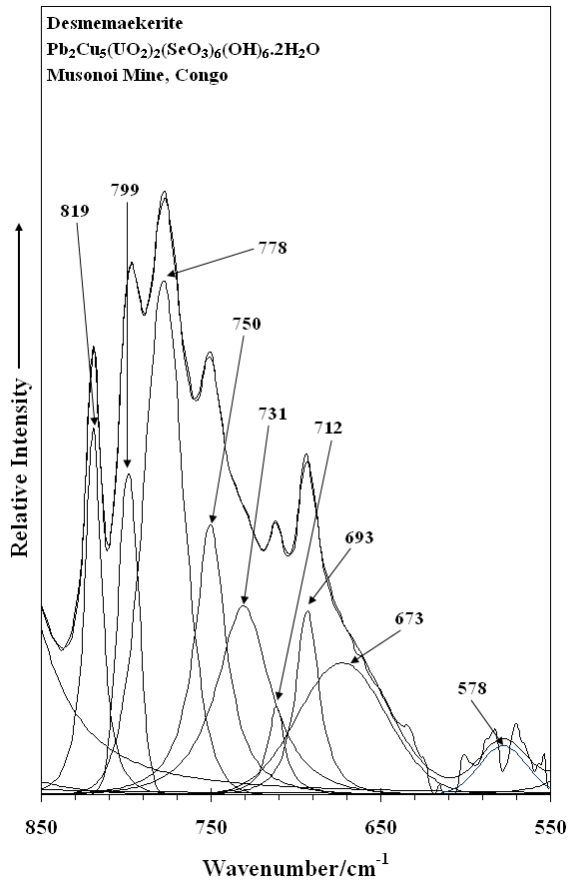
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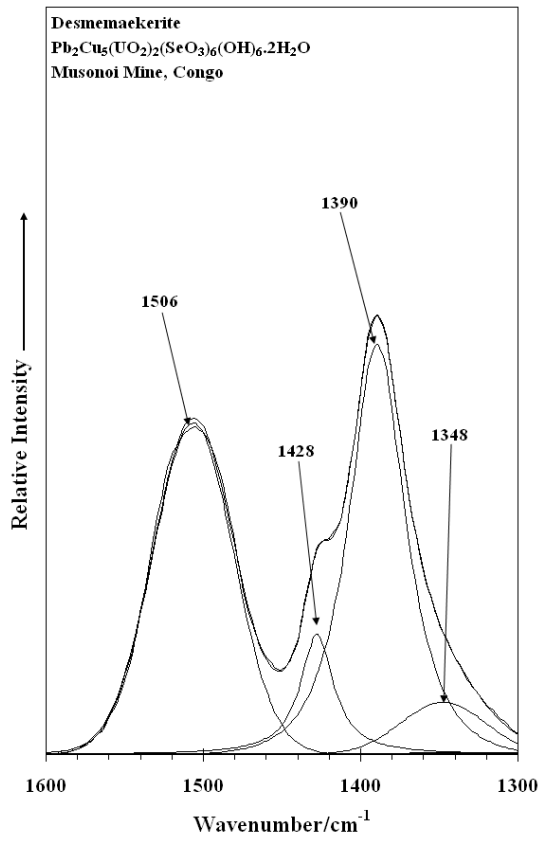
308 **Fig. 4**



309

310

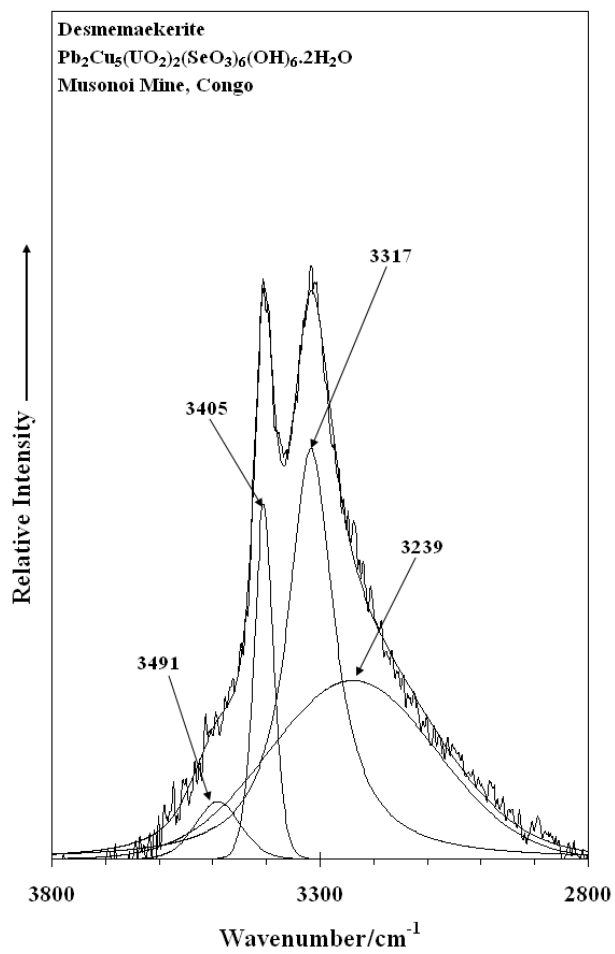
311 **Fig. 5**



312

313

314 **Fig. 6**



315

316 **Fig. 7**